spinning bath neutralizes free NaOH and decomposes xanthate and various viscous by-products containing sulfur, thus liberating CS_2, H_2S, CO_2, and S. Salts such as $ZnSO_4$ and Na_2SO_4 coagulate the xanthate, forming relatively stable metal complexes. The sulfuric acid/salts ratio is a key control point, which, although coagulation and regeneration take place together, ensures that the xanthate gels before the acid can attack and decompose it. Four percent or more glucose prevents crystallization of salts in the filaments.

Three separate continuous spinning and treating procedures are outlined in Fig. 35.7.

1. Textile yarns are twisted into continuous yarn as the filaments leave the spinneret. They are dyed (then or later) and sent to coning and warping.
2. Tire yarns are stretched to impart strength over a series of thread-advancing rolls where wash and other treatments are applied, such as deacidifying, desulfurizing, and bleaching.
3. Staple yarns are spun on the machine in the lower part of Fig. 35.7 by combining filaments from many spinnerets without twisting and cutting them into uniform lengths. Each year more viscose filaments are made into staple fiber.

The actual process of continuous spinning has reduced the elapsed time from hours to minutes. The types of machines in general use are continuous, bucket, and bobbin. Three-quarters of U.S. production is from the long-used bucket type (Fig. 35.8). If a bucket machine is used, the spinneret head dips horizontally into the spinning solution, and several of the filaments are gathered into a thread and fed down to a small centrifugal bucket spinning at about 7500 rpm. The bucket imparts one twist to the filaments per revolution and removes a greater portion of the occluded bath liquor through perforations in the periphery.

If a bobbin machine is used, the spinnerets point vertically upward into the spinning bath, and the filaments are wound on a revolving bobbin. No twist is imparted to the thread.

Yarn from either type is washed to remove the spinning liquor and desulfurized by treating with a 1% sodium sulfide solution. They are then washed in hypochlorite solution, washed again in water, dried, and coned.

Originally rayon filaments had a cylindrical cross section and a silky appearance and feel. In an effort to produce a rayon that is more like cotton, the shape of the fiber has been modified. Avril III and Avril-Prima are highly crimped, very high wet modulus fibers that have irregularly shaped cross sections and have many cottonlike properties.[17]

CELLULOSE ACETATE MANUFACTURE. Cellulose acetate and its homologs are esters of cellulose and are not regenerated cellulose. The raw material for the spinning solution is prepared by charging acetic anhydride, glacial acetic acid, and a small quantity of sulfuric acid as a catalyst to a jacketed, glass-lined, agitated, cast-iron acetylator (see Fig. 35.9). The mixture is cooled to 7°C, and the wood pulp is added slowly. The acetylation requires 5 to 8 h, and the temperature is maintained below 50°C. The viscous fluid is diluted with equal parts of concentrated acetic acid and 10% sulfuric acid and allowed to age for 15 h at 38°C. Hydration of some of the acetate groups occurs. No method has been devised whereby cellulose can be converted directly to a product of the desired acetyl content. It is necessary to transform it first to the triacetate and partly hydrolyze off the required proportion of acetate groups. The desired material is usually about half way between triacetate and diacetate.

The hydration is stopped by running the mixture into a large volume of water and precipitating the secondary acetate. The secondary acetate is centrifuged to separate it from the still strong acetic acid which is recovered, concentrated, and used over.

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[17]A Rayon Rebirth, *Chem. Eng.* **86** (7) 113 (1979).
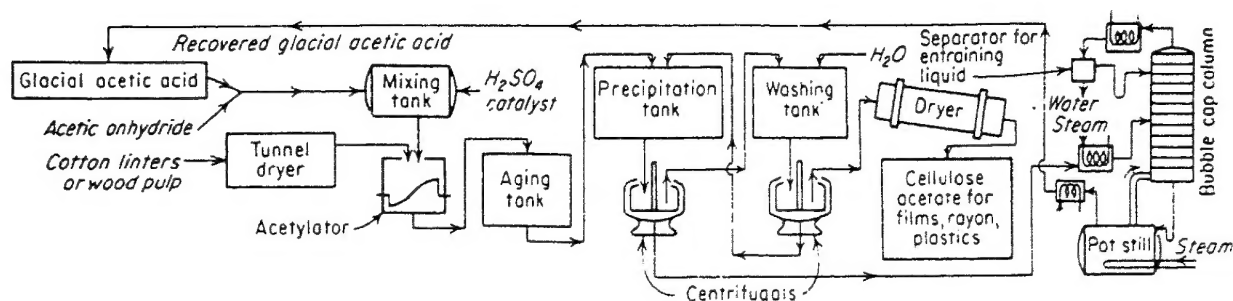
In order to produce 1 kg of acetate rayon the following materials and utilities are required.

Pulp	0.70 kg	Sulfuric acid	0.1 kg
Acetic anhydride	0.2 kg	Direct labor	0.09 work-h
Acetic acid	3.25 kg	Acetone loss	0.2 kg

Fig. 35.9. Flowchart for cellulose acetate manufacture.

The flakes are washed several times by decantation and are then ready to be used in preparing the spinning solution by dissolving the dry flakes in acetone in a closed, agitated mixer. If desired, a delustering pigment is added. Several batches are blended, filtered, and sent to the spinning machine. The solution is forced through spinnerets into a current of warm, moist air. The acetone evaporates and is recovered, leaving a filament of cellulose acetate.

These filaments are twisted and coned in the same manner as those of the previously described rayons. Some yarns are sold without a twist. Filament yarn is made by twisting the threads before winding on the bobbin. Tow consists of threads gathered without twisting and is cut into short lengths for use as staple fibers.

The economical operation of the process depends on the recovery of as many of the chemicals as possible. For every kilogram of cellulose acetate about 4 kg of 30 to 35% aqueous acetic acid is obtained. Dilute acetic acid from various parts of the process is run through a thickener to remove the last traces of cellulose acetate and then concentrated in a distilling unit and reconverted to acetic anhydride. The acetone-laden air from the spinning machines may be passed through activated charcoal to absorb the solvent (which is subsequently recovered by steaming and rectification) or by cooling the air in water towers and simultaneously dissolving out the acetone, the water-acetone mixture later being rectified. Liquid absorption and distillation are also employed.

Cellulose triacetate fiber, Arnel, is made by Celanese Corp. It is reported to possess resistance to glazing at high ironing temperatures, complete machine washability, low shrinkage in stretching, good crease and pleat retention, and an adaptability to a wide range of colors, designs, and prints.[18] It is prepared by dissolving the triacetate in dichloromethane instead of acetone as is used for the diacetate.

CARBON FIBERS[19]

High-modulus carbon fibers are prepared from rayon, polyacrylonitrile (PAN), or pitch. Rayon fibers are charred at 200 to 350°C and then carbonized at 1000 to 2000°C. The result-

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[18]Moncrieff, op. cit.

[19]ECT, 3d ed., vol. 4, 1978, p. 622; Delmonte, *Technology of Carbon and Graphite Fiber*

ing carbon fibers are then heat treated at 3000°C and stretched during the heat treatment. This is a very costly process as the overall yields are only about 25 percent. These rayon-produced fibers are used for manufacturing heat shields for aerospace vehicles, and for aircraft brakes.

Fibers can be produced from PAN in a better yield, but the Young's modulus is not as high as those prepared from rayon. The PAN is stretched 100 to 500 percent at 100°C, heated at 190 to 280°C for 0.5 to 5 h, and then carbonized at 1000 to 1300°C. The yield is about 45 percent. The modulus can be increased by heating above 2500°C.

Coal tar or petroleum pitch is first heated to form a liquid crystal state (mesophase). Yarn is spun from the liquid and thermoset in an oxygen atmosphere. When heated to 3000°C the fibers have a high modulus and require no costly stretching.[20]

Carbon fibers are sold in three forms:

1. *Low modulus (138 GPa) mat.* This is used as an electrically conducting surface for electrostatic spraying and in injection molding to get electrical conductivity, resistance to heat, and improved wear (for bearings).

2. *Medium modulus (138–517 GPa).* This fiber can be formed into fabrics.

3. *High-modulus (above 345 GPa).* This is the lowest priced high-modulus yarn available and is used when stiffness is critical.

Carbon fibers are used for reinforcing plastics which can be used for sporting goods (fishing rods, etc.) and engineering plastics.

FINISHING AND DYEING OF TEXTILES

Many of the textile industries mill operations abound in chemical engineering problems. Dyeing, bleaching, printing, special finishing (such as for crease recovery, dimensional stability, resistance to microbial attack and ultraviolet light), flame resistance, scouring, water treatment, and waste disposal are examples of mill treatments where unit operations as filtering, heating, cooling, evaporation, and mixing are involved.

The modification[21] of fibers and fabrics by special treatments to change their properties and to improve their usefulness is increasing. Three important finishes consist of flameproofing or fire retarding, mildew or rotproofing, and water repellency. Temporary flame proofing of cellulosic fibers is achieved by the application of ammonium salts or borax and boric acid. Ideal fabric flame proofing, which allows cleaning or laundering and yet maintains desirable fabric characteristics is difficult, although much research is directed toward this aim,[22] and some processes are finding commercial acceptance. Mildew proofing of cellulosic fabrics may be obtained by the use of many organic and inorganic compounds. Commonly used materials include acrylonitrile, chlorinated phenols, salicylanilide, and organic mercurial compounds. copper ammonium fluoride, and copper ammonium carbonate. To produce water-repellent finishes durable to the usual cleaning processes, special quaternary ammonium compounds are heat-treated onto the fiber. Shrink proofing of wool employs various chlorinating processes, especially for socks, shirts, knitting yarns, and blankets. Another method for shrink

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[20]Barr et al., High Modulus Carbon Fibers from Pitch Precursor, New and Specialty Fibers. Applied Polymer Symposia No. 29, ACS, Columbus, Ohio, 1975.

[21]For Fibers, Finish Is Just the Start, *Text. World* 129 (7) 341 (1979).

[22]See Chap. 16.

proofing woven fabrics is to coat them with a melamine-formaldehyde product. Thermosetting resins are being widely used to impart crease or wrinkle resistance to cellulosic fibers. Commonly used products include urea-formaldehyde and melamine-formaldehyde resins. The fabric is treated with water-soluble precondensates, together with a condensation catalyst. The treated fabric is dried and heated at an elevated temperature to set the resin within the fiber structure. Many other special treatments for fabrics include mothproofing, improving of resiliency, stiffening, softening, eliminating electrostatic charge during processing, sizing, lubricating, and inhibiting atmospheric gas fading of dyes. In recent years chemical finishes have been used to react with the fiber material, e.g., cotton, and thereby to change its properties by esterification (carboxymethylation) or amination (2-aminosulfuric acid).

FILMS[23]

The first successful plastic film was cellulose nitrate. This was soon followed by regenerated cellulose and cellulose acetate. Up until 1950 regenerated cellulose film had the largest share of the market. The advent of polyethylene was the first to challenge cellulose's supremacy. Now films are produced from other polyolefins, polyvinyl chloride and acetate, polystyrene and polystyrene copolymers, and polyamides, polycarbonates, acrylics, and many other polymers.

VISCOSE AND CELLULOSE ACETATE. Transparent viscose film (Cellophane) is manufactured from a solution similar to that used for rayon. The solution is extruded through a slit-die into a coagulating bath of buffered sulfuric acid and cast as a sheet upon a rotating drum, the lower side of which is submerged in the bath. The viscose film formed is transferred to succeeding tanks of warm water to remove the acid. It is desulfurized in a basic solution of sodium sulfide and rewashed. The characteristic yellow color is removed by a hypochlorite bleach, washed thoroughly, and the sheet is then infused with glycerol to impart plasticity to the film. Uncoated cellulose film is not moisture-proof and its packaging uses are limited. It does not seal on automatic machinery, it shrinks on getting wet, and does not prevent moisture loss. It is used for sausage casings, as a base for pressure-sensitive tapes (the adhesives are acrylic copolymers), and as a release agent in molding resins. One great advantage is that it is biodegradable.

Moistureproof cellulose films are prepared by coating one side with nitrocellulose lacquer or a polyvinylidene chloride copolymer solution. The coated films can be printed, and are still biodegradable, although the time required is a little longer.

The manufacture of transparent cellulose acetate sheeting comparable with cellophane is by extrusion of an acetone solution of the required properties through a narrow slit onto a rotating drum, where, in the presence of warm air, the acetone solvent evaporates. The resulting sheet is pliable and moistureproof and is used for photographic film.

POLYOLEFINS. Polyethylene films are made by melting the polymer and extruding it by either slit-die or blow extrusion. The slit-die process produces flat sheets of film by extruding

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[23]Briston and Katan, *Plastics Films*, Wiley, New York, 1974; Oswin, *Plastic Films and Packaging*, Wiley, New York, 1975; Nass (ed.), *Encyclopedia of PVC*, Marcel Dekker, New York, 1977.

the molten polymer through a slit-die into a quenching water bath or onto a chilled roller. It is essential that the film be cooled rapidly to form only small crystals and thus maintain its clarity. Very high outputs of film with superior optical properties can be obtained by this method.

The blow extrusion process produces tubular film by using air pressure to force the molten polymer around a mandrel. The plastic emerges from the die through a ring-shaped opening in the form of a tube bubble. The extrusion is usually upward, but it can be down or even horizontal. Figure 35.10 shows the main features of the blow extrusion process. Polypropylene film cannot be formed by this air-cooled method because its rate of cooling is too slow and thus large crystalline aggregates are formed. A water-cooled tubular process[24] has been developed that produces clear polypropylene film at about the same cost as cast film.

POLYVINYL CHLORIDE. PVC film is prepared by feeding a plastic mix of polymer, stabilizers, and plasticizers between two heated rolls where it is squeezed into a film. This process is known as calendering and is widely used in the rubber industry (Chap. 36). Calendering produces sheets of better uniformity of thickness compared with extruded sheets. PVC requires plasticization because without a plasticizer the films are very brittle. The simple phthalates are most commonly used for this purpose and often in amounts up to 50 parts per hundred parts resin (phr). Dioctyl phthalate is the lowest weight member of the series that has low enough volatility to be used. This gives a general purpose film which, however, becomes brittle at very low temperatures. Films for low-temperature use are made using aliphatic esters, such as di-2-ethylhexyladipate, for plasticizers. Different plasticizer content

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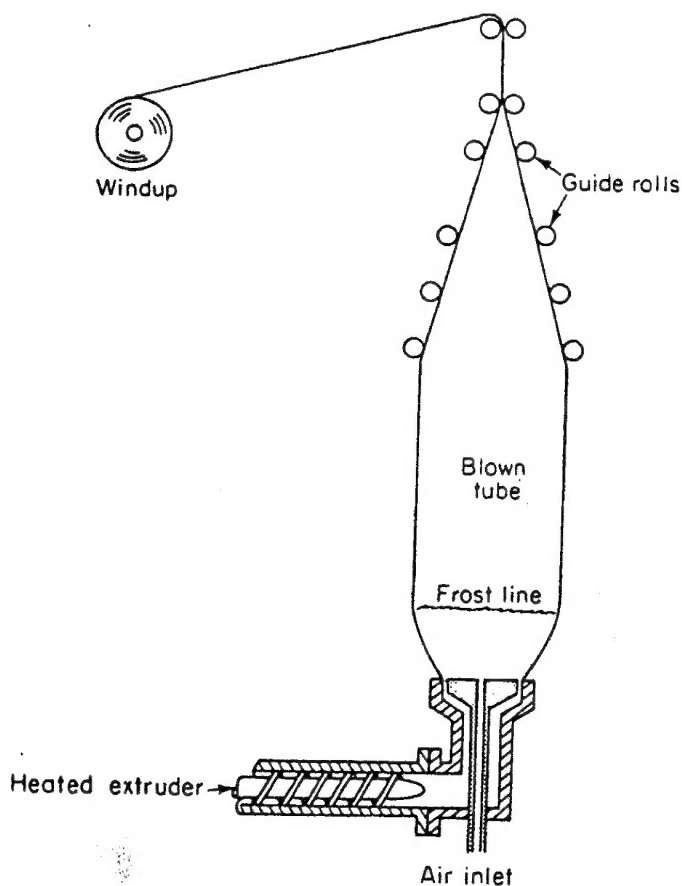[24]Prall, Cooling Blown Tubular Film, *Modern Plastics* 46 (4) 154 (1969).

Fig. 35.10. Blown film extrusion process.

produces a range of films suitable for different wrapping applications. Meat wraps require very high concentrations to resist moisture and oxygen. PVC films are not biodegradable and give off HCl when burned thus making environmentally acceptable disposal difficult.

OTHER POLYMERS. Almost any thermoplastic resin can be formed into film by the use of one or the other of the processes described. The choice of process depends largely upon the physical properties of the resin. Polyester and polyamide films are melt extruded. Table 35.1 gives the trade names of some of the common films.

SELECTED REFERENCES

Briston, J. H.: *Plastics Films*, Wiley, New York, 1974.

Chapman, C. B.: *Fibres*, Butterworths, London, 1974.

Delmonte, J.: *Technology of Carbon and Graphite Fiber Composites*, Van Nostrand Reinhold, New York, 1981.

Economy, J.: *New and Specialty Fibers*, Wiley, New York, 1976.

Jones, H. R.: *Pollution Control in the Textile Industry*, Noyes, Park Ridge, N.J., 1973.

Lowenstein, K. L.: *The Manufacturing Technology of Continuous Glass Fibers*, American Elsevier, New York, 1973.

Moncrieff, R. W.: *Man-made Fibres*, 6th ed., Wiley, New York, 1975.

Nass, L. I.: *Encyclopedia of PVC*, Marcel Dekker, New York, 1977.

Oswin, C. R.: *Plastic Films and Packaging*, Wiley, New York, 1975.

Placek, C.: *Multicomponent Fibers*, Noyes, Park Ridge, N.J., 1971.

Robinson, J. S.: *Fiber-Forming Polymers*, Noyes, Park Ridge, N.J., 1980.

Sweeting, O. J.: *The Science and Technology of Polymer Films*, Wiley, New York, 1968.

Chapter 4

Petroleum Processing

Petroleum, the product of natural changes in organic materials over millennia, has accumulated beneath the earth's surface in almost unbelievable quantities and has been discovered by humans and used to meet our varied fuel wants. Because it is a mixture of thousands of organic substances, it has proved adaptable to our changing needs. It has been adapted through changing patterns of processing or *refining*, to the manufacture of a variety of fuels and through chemical changes to the manufacture of a host of pure chemical substances. the petrochemicals.

HISTORICAL. In the United States, Indians used oil seepages in Pennsylvania as medicines. and worldwide, various bitumens were known in Biblical times. Moses' burning bush may well have been an accidentally ignited gas vent. Drake's crude oil well, completed in 1859. showed the world the existence of extensive underground reservoirs of material then mainly useful as a source of kerosene for illuminating lamps. The useless gasoline. which at times had been towed out to sea and burned as a nuisance, gradually became the major product with demand exceeding the supply. Improved quality, as represented by antiknock value, was also desired. The available quantity was extended by converting less desirable fractions into gasoline, first by thermal, later by catalytic cracking processes. Quality improvement in gasoline was brought about by cracking, the tetraethyl lead antiknock properties discovery. polymerization, alkylation, aromatization, and through the gradual awareness that transformations of many kinds were possible by the application of organic processes on a large scale.

Refining has always been pushed along reluctantly by economic factors. For years, many companies viewed refining as a necessary evil to be endured so that they could make money from the more vital production and sale of the crude oil which they produced. Only recently, most companies have come to realize that their purpose is to take a many-component raw material and convert it, at maximum profit, into materials to fulfill the needs of a complex and constantly shifting multiproduct market. In 1930, a company could market only gasoline. kerosene, heating fuel, gas oil, and residuum and show a profit. Today the market is far more complicated, and the marketing decisions are more difficult. Simple fractionation of crude oil into fractions was once sufficient but such simple products would rarely be salable now. Quality needs require upgrading, blending, and consistent quality control of the finished products. although the crudes refined may vary greatly in type and distillate content.

The United States is the largest consumer of petroleum products in the world and has the greatest refining capacity[1] (2,763,800 m^3/day), but is no longer self-sufficient in raw material. The petroleum industry in its design, operation, sales, and executive branches is the largest

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[1]Refining capacity is usually stated in U.S. barrels of crude processed. A barrel of oil is 42 U.S. gallons = 0.159 m^3. The capacity figure is from *Hydrocarbon Process*. 61 (9) 13 (1982) and includes 350,000 m^3 of capacity of units in operable shutdown.

employer of chemical engineers. Refining processes have become extremely large and quite complicated. All the branches of this industry are so interrelated and technical that engineering training is required at every level. Needs for technical help are also being enlarged because: (1) sudden price increases for crude and changing markets have required extensive technical readjustment designed to make better use of an expensive and increasingly scarce commodity and (2) the industry has expanded into many other chemical fields—including supplying raw materials formerly supplied by other, smaller sources.

Chemical engineering and petroleum processing have in a very real sense grown up together. Studies on fluid flow, heat transfer, distillation, absorption, and the like were undertaken and applied to a wide variety of materials because of need in the petroleum processing field. Since refined products have physical properties which vary widely from those of water, theory has been refined to include these variables, thus expanding the scope of chemical and mechanical engineering science.

Early refineries used batch stills, small horizontal cylinders, with little or no differential distillation to separate the components, and a condenser. This equipment was originally developed for distilling alcohol. The still produced first gas, then gasoline, then a series of oils of increasing average boiling points and lower value, until a heavy lubricating oil, or asphalt (depending upon the type of crude charged) remained in the still. Modern units operate continuously. First a tubular heater supplies hot oil to an efficient distillation column which separates the material by boiling points into products similar to those obtained with the batch still, but more cleanly separated; then later units convert the less salable parts of the crude (the so-called bottom half of the barrel) into desired salable products. The processes used include various cracking units (which make small molecules from large ones), polymerization, reforming, hydrocracking, hydrotreating, isomerization, severe processing known as coking, and literally dozens of other processes designed to alter boiling point and molecular geometry.

ORIGIN.[2] Most theories concerning the origin of petroleum postulate a vegetable origin with a close relationship to coal. Theory holds that any organic matter may be converted into petroleum under suitable conditions. There is also general agreement that petroleum was formed from organic matter near shore and in marine deposits deficient in oxygen and associated with minerals converted by time and pressure into limestones, dolomites, sandstones, and similar rocks. The concentration of organic matter in the original deposits may not have been high, but petroleum gas and liquids have migrated and gathered in places favoring retention, e.g., sealed-off porous sandstones. Over long periods of time,[3] carbohydrates and proteins are probably destroyed by bacterial action leaving the fatty oils which are more refractory to bacterial or chemical destruction.

EXPLORATION. At one time drilling for petroleum was a hit-or-miss affair and only 1 out of 100 wildcat[4] wells struck oil. Geophysical and seismic work has become highly refined, and when combined with high-speed computers to evaluate the vast amount of data used to locate sites, the chance of drilling success has greatly increased. Geologists and geophysicists studied

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[2]*Science of Petroleum*, vol. 1, 1938, p. 52; Tissot and Welti, *Petroleum Formation and Occurrence*, Springer Verlag, New York, 1978.

[3]Andreev, Bogomolov, Dobryanskii, and Kartsev, *Transformation of Petroleum in Nature*, Pergamon, Oxford, 1968.

[4]A wildcat is a well in an untested area whose location is determined with little scientific assistance.

the occurrence of oil and used scientific instruments to direct their recommendations unti by 1962, 1 out of 9 wells drilled produced either oil, gas, or both. Today's success rate is eve better. Discoveries are now being made in previously explored and rejected areas of difficu geology, such as the Rocky Mountain overthrust area, and the success rate remains high.

Geologists recognized at an early date that petroleum accumulates in pools caught in th anticlinal folds of sedimentary rocks. The gradual accumulation of data from drilling core has guided the test procedures. At scientifically selected sites, wells have been drilled deepe than 6500 m to reach gas or oil.

Seismic analysis can determine the presence of domes and deposits at a considerable dept below the surface. The top of the arch of an anticline or dome is compressed and has a greate density than the surrounding rocks. Figure 37.1 shows the various strata surrounding oil-beai ing rock or sand. Oil and salt also have lower densities than the surrounding rocks. Creatin small seismic waves and measuring their reflected waves at intervals in space and time make possible accurate gravimetric mapping. The finding of a new field is a most serious and exper sive undertaking.

PRODUCTION STATISTICS. The free world's consumption of petroleum in 1982[5] was 2.69 > 10^9 m^3, down from the 1979 peak of 3.04 × 10^9 m^3. Total world consumption was estimate at 5.59 × 10^9 m^3/year. U.S. oil fields produce approximately 14 percent of the world's petrc

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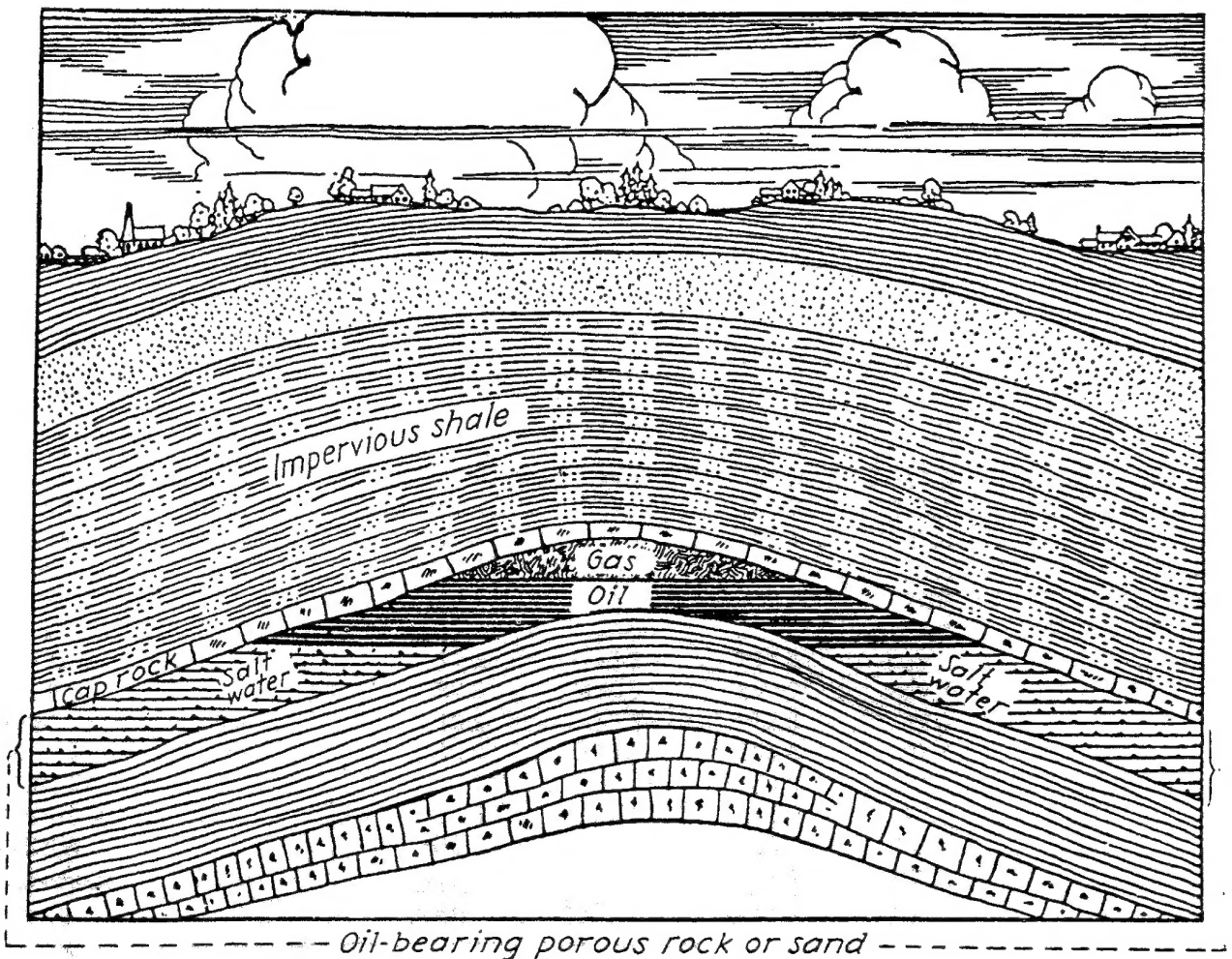[5]*World Energy Outlook*, Standard Oil of California, 1982.

Fig. 37.1. Oil trapped in nature's reservoir. (*American Petroleum Institute.*)

leum as shown in Table 37.1. Most of the free-world fields, except those of OPEC (Organization of Petroleum Exporting Countries), are currently producing at maximum rates. No industry publishes more extensive statistical data than does the petroleum industry through the API (American Petroleum Institute) and other data-collecting agencies.[6] Table 37.2 shows the quantities of refined products currently produced in the United States. Table 37.3 shows the petroleum industry expenditures for new plants and equipment. It is felt that gasoline consumption in the United States has now peaked, so the major new growth will be in the consumption of diesel fuel and kerosene-based jet fuels until these last two will exceed gasoline.

OPEC now provides 50 percent of the total free-world oil production. By 1990,[7] this should be somewhat less as new fields are found in other locations, and as OPEC reaches productive maturity.

RESERVES AND RAW MATERIALS. Estimates of the reserves of such essential minerals as petroleum are inexact, but of vital importance in predicting future trends and in planning.

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[6]See various publications by the API and other industry organizations.
[7]*World Energy Outlook*, op. cit.

Table 37.1 World Crude Oil Production by Countries and by Years (in millions of cubic meters; to convert to U.S. barrels multiply by 6.33)

	1977	1978	1979	1980
Algeria	66.5	67.0	66.5	62.9
Argentina	24.8	26.1	27.2	29.1
Australia	24.8	25.0	25.2	22.1
Brazil	9.3	9.3	9.8	10.7
Canada	76.1	75.5	86.1	83.7
China, mainland	108.1	120.1	122.5	122.0
Ecuador	10.6	12.3	12.3	12.3
Egypt	23.9	27.8	28.4	34.0
India	12.0	13.1	14.9	12.6
Indonesia	97.2	94.3	95.0	84.8
Iran	326.6	302.2	177.1	86.9
Iraq	135.4	147.7	197.8	151.8
Kuwait	113.6	122.9	144.3	95.1
Libya	119.0	113.9	119.1	103.3
Malaysia	10.6	12.5	16.3	15.8
Mexico	56.6	69.7	84.2	111.9
Nigeria	120.1	110.1	148.7	119.1
Norway	16.1	20.1	22.1	28.8
Oman	19.6	18.2	17.1	16.6
Peru	5.2	8.7	11.1	10.9
Qatar	25.6	28.0	29.3	27.3
Rumania	17.2	16.3	14.5	13.6
Saudi Arabia	530.6	478.7	549.7	557.7
Trinidad and Tobago	13.3	13.3	12.3	12.3
United Arab Emirates	115.3	105.5	104.8	98.6
United Kingdom	44.1	61.5	88.8	91.8
United States	475.4	502.1	492.0	497.1
U.S.S.R.	633.7	663.8	680.0	700.3
Venezuela	129.1	124.8	135.9	125.3
Total	3360	3391	3533	3338

Table 37.2 U.S. Refinery Production (in millions of m³; to convert to U.S. barrels, multiply by 6.33)

Product	1965	1975	1978	1979	1980
Still gases°	14,170	17,840	20,388	20,898	20,082
Liquefied refinery gases	17.0	17.3	19.9	19.2	18.9
Gasoline	269	380	418	399	380
Petrochemical feedstocks	9.2	19.4	35.5	40.0	38.0
Kerosene	14.8	8.7	8.9	10.7	7.9
Jet fuel	30.4	50.6	56.3	58.7	58.0
Distillate fuel oil	122	154	184	183	157
Residual fuel oil	42.8	71.7	96.8	97.9	94.8
Asphalt	19.7	22.9	27.5	26.9	22.4
Coke, metric tons	18.9	28.4	29.7	30.1	29.7
Other finished products	38.8	20.8	26.5	25.1	18.6

°In cubic meters of gas (10^3 m³ = 1.04 t). Calculated from data in *Statistical Abstract of the United States*. 1981.

To make such statistics more reliable, it is customary to use the term "proved reserves" to refer to minerals known to exist in well-defined fields and which are recoverable by present production methods. Not all the petroleum existing underground is recoverable. Heavy crude recovery seldom exceeds 50 percent. Under favorable circumstances, up to 80 percent of lighter crudes may be brought to the surface. Although some is wasted, practically all natural gas can be recovered and utilized. Proved reserves of the world in 1981 were estimated at 1.03×10^{11} m³ of which the proved reserves in the United States constituted 4.20×10^9 m³

The actual useful size of reserves is dependent upon the recovery techniques used. Ashburn. in 1887, estimated that wasteful production techniques in Pennsylvania and New York oil fields would ultimately result in the recovery of only 11 to 12 percent of the oil present. If methods now available had been used then, 2 to 2½ times more oil would have been taken out than was actually recovered by natural flow and pumping. The key to the problem is proper conservation and utilization of reservoir energy. Oil is usually underlaid with water under considerable pressure and overlaid with gas, as shown in Fig. 37.1. Withdrawal of oil from the proper place at a sufficiently low rate allows the pressure to be maintained, saving much pumping energy.

Natural gas or CO_2 can be returned to repressure wells. In one instance, a slower rate of oil production and recycling natural gas at 9.6 MPa enabled a net recovery of 70 percent of the oil originally present. This is twice the amount recoverable without repressuring. Natural high-pressure CO_2 is often piped long distances to use in oil fields. Air is not suitable for repressuring, because it causes deterioration in the quality of the oil produced.

Table 37.3 Petroleum Industry Expenditures for New Plants and Equipment (in dollars $\times 10^9$)

Function	1960	1970	1975	1980	1981
Production	1.6	2.0	4.6	11.3	13.4
Transportation	0.2	0.4	0.8	1.0	1.1
Refining and petrochemicals	0.5	1.3	2.6	4.6	5.8
Marketing	0.5	1.0	0.5	0.9	0.8
Other	0.1	0.5	1.1	2.8	4.1
Total	2.9	5.2	9.6	20.6	25.2

SOURCE: *Statistical Abstract of the United States*, 1981.

Water introduced into a central well can force oil out to surrounding wells. Such *water flooding* is extensively practiced. Some abandoned areas have been made into good producers by this technique.

Steam flooding is in extensive use in some heavy crude oil fields. The addition of heat and or surface-active materials and polymers *(micellar flooding)* also contribute to better recovery. Such treatments are expensive. Underground combustion of some of the oil to heat up the rest so that it will flow more readily is an established method. "Operation Plowshare" tested a nuclear explosion to release natural gas from rock. It was a modest technical success. but an economic failure.

For years, wells drilled into hard limestone have been shot with nitroglycerin because the resulting fissures and fractures increased the drainage of oil into the reservoir. Hydraulic fracturing with gels containing solid propping agents to hold the formed fissures open is much in vogue. The Plowshare explosion was an extension of the idea of opening channels in otherwise relatively impervious materials. Today, almost every well drilled into a limestone formation has the drainage channels enlarged by treatment with inhibited (to prevent iron corrosion) hydrochloric acid. Explosive treatment followed by acid treatment is also common. The oil service industry has grown to meet these problems,[5] which are distinctly different from drilling problems. This technically oriented group has become a major user of hydrochloric acid and a great many other chemicals. Some fields do not produce at all until after treatment The movement of oil underground is controlled by its viscosity and surface tension. Gas dissolved in the oil reduces both, another reason to maintain reservoir pressure, since increased gas pressure means more gas dissolved and better fluid properties.

Offshore drilling has resulted in many new wells and is becoming increasingly important as as an area promising new fields after the present ones are gone.

TAR SANDS.[9] Canadian tar sands are being worked to produce a heavy crude. but processing difficulties due to the arctic environment and excessive government interference have made the enterprise a technical success but marginal economically. Major tar sands deposits exist in the United States in California, Kentucky, Texas. and Utah. Canadian reserves have been estimated to contain 6.3×10^{10} m^3 of heavy crude; the United States has 5.69×10^9 m^3 with only about 15 percent recoverable with current methods and at current prices. Several small pilot units are testing technology and the market. Most recover the crude by steaming.[10] Ultrasonics are also being applied.

OIL SHALE. The oil in tar sands is merely mixed with the sands, but in shale the oil is chemically combined with the rock material forming an entity known as kerogen. Kerogen reluctantly gives up its heavy oil which contains higher percentages of nitrogen and sulfur than ordinary crude. Many processing methods have been suggested and several piloted. Klass[11] summarizes them.

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[5]Mathews, The Challenge of Oil Field Chemicals. *CHEMTECH* 10 (12) 756 (1980).

[9]McIntyre, Giant Oil Plant Comes on Stream, *Chem. Eng.* 85 (20) 123 (1978); Oil Recovery Is Higher in New Tar-Sands Route, *Chem. Eng.* 87 (25) 37 (1980).

[10]Chilingarian and Yen (eds.): *Bitumens, Asphalts, and Tar Sands,* Elsevier, New York. 1978.

[11]Klass, Synthetic Crude Oil from Shale and Coal, *CHEMTECH* 5 (8) 499 (1975); Parkinson, New Ways to Process Oil Shale, *Chem. Eng.* 89 (4) 37 (1982).

The difficulties in commercializing a shale oil process are formidable.[12] Each ton of rock processed yields less than 0.2 m^3 of oil, leaving a great volume of solid to be disposed of. The solids contain soluble constituents such as trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$), nahcolite ($NaHCO_3$), dawsonite [$Al_2(CO_3)_3 \cdot Na_2CO_3 \cdot nH_2O$], and halite ($NaCl$). While these materials have value, they are in crude form, and at present they are mainly a difficult disposal problem. Table 37.4 shows the reason for the continued interest in this major national resource.

Major shale deposits occur in Colorado, Utah, and Wyoming with scattered smaller deposits in the eastern states of Indiana, Kentucky, Ohio, and Tennessee. Most deposits are on government-owned land in arid regions. To properly evaluate the commercial promise of shale oil, mining and processing methods must be put into motion to produce at least 5000 to 8000 m^3/day of crude to run over a period long enough to permit full return on the investment (20 to 30 years). Such enterprises cost several billion dollars. Several groups have started and later abandoned projects, but about a half-dozen projects appear likely to be put into production soon, marking the start of a real shale-oil industry. The OPEC oil price increase has made consideration of plants now economically possible. In situ processing and several new mining-retorting processes are under study.[13] The following processes currently command attention, each (except Nos. 4 & 5) can be applied to raw or beneficiated rock.

1. Solids-to-solids heating.
2. Gas-to-solids heating with internal gas combustion.
3. Gas-to-solids heating with external heat generators.
4. In situ retorting with combustion heating.
5. In situ retorting with radio-frequency heating.

With all the attention now being given to the problem, it seems certain that a new industry is about to be created here, but when, and how, it will become economically viable is impossible to predict.

TRANSPORTATION. In the United States a great pipeline transportation system moves a tremendous tonnage of petroleum and natural gas. The pipeline has reached its maximum application east of the Rocky Mountains, where trunk lines, branch lines, and pumping stations form an extremely complex system. The pipeline is the most economical method for trans-

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[12]Taylor, Oil Shale Commercialization: the Risks and the Potential, *Chem. Eng.* 88 (18) 63 (1981).

[13]Parkinson, New Ways to Process Shale Oil, *Chem. Eng.* 89 (4) 37 (1982).

Table 37.4 Fossil Fuel Resources of the United States (in EMJ, 10^{18} MJ)

	Estimated in Place	Known or Proved Recoverable
Coal	34.8	8.63
Shale oil and bitumens	9.52	0.48
Natural gas and natural gas liquids	2.93	0.33
Crude oil	2.53	0.23
Total	49.8	9.67

SOURCE: Calculated from data in Klass, Synthetic Crude Oil from Shale and Coal, *CHEMTECH* 5 (8) 499 (1975).

porting natural gas. At regular intervals pressure-booster stations are located, using a small part of the gas to drive gas engines connected to compressors.

The United States has at present over 313,000 km of petroleum pipelines and 1,691,000 km of natural-gas lines.

The growth in use of foreign crude oil has spawned a great shipping industry which has constructed mammoth tankers, some as big as 400,000 deadweight metric tons and carrying over 500,000 m^3 of crude. Refined products are also carried by pipelines, barges, railroad tank cars, and motor tank trucks. Storage of products, some of them under high pressure and all of them highly flammable, has been standardized until now the fire hazard is quite small. Some LPG (liquefied petroleum gas) is stored underground.

CONSTITUENTS OF PETROLEUM

Crude petroleum is made up of thousands of different chemical substances including gases, liquids, and solids and ranging from methane to asphalt. Most constituents are hydrocarbons, but there are significant amounts of compounds containing nitrogen (0 to 0.5%), sulfur 0 to 6%), and oxygen (0 to 3.5%).[14]

The API has joined other groups in an extensive and expensive study to identify the actual constituents of petroleum and has identified over 200 compounds.[15] In the following section, an attempt is made to give some idea of the quantities of a given identified compound contained in several different U.S. crudes. The figures given are volume per volume percentages for (in order) Ponca, Okla. (PO), East Texas (ER), and Bradford, Okla. (BO), crudes which have been studied extensively. No one constituent exists in large quantity in any crude

ALIPHATICS, OR OPEN CHAIN HYDROCARBONS

n-Paraffin Series or Alkanes, C_nH_{2n+2}. This series comprises a larger fraction of most crudes than any other. Most straight-run (i.e., distilled directly from the crude) gasolines are predominantly n-paraffins. These materials have poor antiknock properties. Examples are n-hexane ($\pm 2\%$ all samples) and n-heptane (PO = 2.5, ET = 1.7, BO = 2.5% v/v). As gasolines, these materials knock badly.

Iso-paraffin Series or Iso-alkanes, C_nH_{2n+2}. These branched chain materials perform better in internal-combustion engines than n-paraffins and hence are considered more desirable. They may be formed by catalytic reforming, alkylation, polymerization, or isomerization. Only small amounts exist in crudes, e.g., 2- and 3-methylpentanes (0.8, 1.5, 0.9%), 2,3-dimethylpentane and 2-methyl hexane (1.2, 1.3, 1.3%).

Olefin, or Alkene Series, C_nH_{2n}. This series is generally absent in crudes, but refining processes such as cracking (making smaller molecules from large ones) produce them. These relatively unstable molecules improve the antiknock quality of gasoline, although not as effectively as iso-paraffins. On storage they polymerize and oxidize, which is undesirable. This very tendency to react, however, makes them useful for forming other compounds, petrochemi-

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[14]ECT, 3d ed., vol. 17, 1982, p. 119.

[15]American Petroleum Institute Research Projects APRIP 6 to 60.

cals, by additional chemical reactions. Ethylene, propylene, and butylene (also called ethene, propene, and butene) are examples. Cracked gasolines contain many higher members of the series.

RING COMPOUNDS

Naphthene Series or Cycloalkanes, C_nH_{2n}. This series, not to be confused with naphthalene, has the same chemical formula as the olefins, but lacks their instability and reactivity because the molecular configuration permits them to be saturated and unreactive like the alkanes. These compounds are the second most abundant series of compounds in most crudes. Examples are methylcyclopentane (0.95, 1.3, 0.5%), cyclohexane (0.75, 0.66, 0.64%), dimethylcyclopentanes (1.75, 2.0, 1.0%), and methylcyclohexane (1.5, 2.4, 2.0%). The lower members of this group are good fuels; higher molecular weight ones are predominant in gas oil and lubricating oils separated from all types of crudes.

Aromatic, or Benzenoid Series, C_nH_{2n-6}. Only small amounts of this series occur in most common crudes, but they are very desirable in gasoline since they have high antiknock value, good storage stability, and many uses besides fuels. A few special crudes (Borneo. Sumatra) contain relatively large amounts. Many aromatics are formed by refining processes. Examples are: benzene (0.15, 0.07, 0.06%), toluene (0.5, 0.6, 0.5%), ethylbenzene (0.15, 0.2. 0.9%), and xylene (0.9, 1.1, 1.0%).

LESSER COMPONENTS. Sulfur has always been an undesirable constituent of petroleum. The strong, objectionable odor of its compounds originally brought about efforts to eliminate them from gasoline and kerosene fractions. Chemical reactions were at first directed at destroying the odor. Later it was found that sulfur compounds had other undesirable effects (corrosion. reducing the effect of tetraethyl lead as an antiknock agent. air pollution). At present. wherever possible, the sulfur compounds are being removed and frequently the sulfur thus removed is recovered as elemental sulfur. Nitrogen compounds cause fewer problems than sulfur compounds, are less objectionable, and are generally ignored.

With the general adoption of catalytic cracking and finishing processes. it was discovered that the occurrence of metals present only in traces (Fe, Mo. Na, Ni, V, etc.) was troublesome as they are strong catalyst poisons. Now methods to remove these substances are being perfected. Salt has been a major problem for many years. It is practically always present in raw crude, usually as an emulsion, and must be removed to prevent corrosion. It breaks down on heating in the presence of hydrocarbons to produce hydrochloric acid. Mechanical or electrical desalting is preliminary to most crude-processing steps.

Petroleum crudes vary widely, each kind requiring different refining procedures. The terms paraffin base, asphalt (naphthene), and mixed base are often applied to differentiate crudes on the basis of the residues produced after simple distillation. A "characterization factor"[16] is also used to describe the properties of a crude with mathematical accuracy.

Pure chemical compounds are not regularly separated by refining processes. Some of the simpler, low molecular weight ones are isolated for processing into petrochemicals. Most petroleum products are mixtures separated on the basis of boiling point ranges and identified by the ultimate uses to which they are well adapted. Figure 37.2 shows the overall relationship between refining processes and refined products.

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[16]Nelson, *Petroleum Refinery Engineering*, 4th ed., McGraw-Hill, New York. 1958